

# Palladium silicide formation under the influence of nitrogen and oxygen impurities

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The effect of impurities on the growth of the  $\text{Pd}_2\text{Si}$  layer upon thermal annealing of a Pd film on  $\langle 100 \rangle$  and amorphous Si substrates is investigated. Nitrogen and oxygen impurities are introduced into either Pd or Si which are subsequently annealed to form  $\text{Pd}_2\text{Si}$ . The complementary techniques of Rutherford backscattering spectrometry, and  $^{15}\text{N}(p,\alpha)^{12}\text{C}$  or  $^{18}\text{O}(p,\alpha)^{15}\text{N}$  nuclear reaction, are used to investigate the behavior of nitrogen or oxygen and the alterations each creates during silicide formation. Both nitrogen and oxygen retard the silicide growth rate if initially present in Si. When they are initially in Pd, there is no significant retardation; instead, an interesting "snow-plowing" effect of N or O by the reaction interface of  $\text{Pd}_2\text{Si}$  is observed. By using N implanted into Si as a marker, Pd and Si appear to trade roles as the moving species, when the silicide front reaches the nitrogen-rich region.

## I. INTRODUCTION

The technological trend of scaling down the device size has made the manufacturing of small area contacts a challenging field of research. Metal silicides have been proposed as the contact material due to their chemical and thermal stability and the selectivity and reproducibility of their Schottky barrier height when making contact to silicon.<sup>1,2</sup> Lateral confinement of contact area exacerbates problems of high-contact resistance and nonuniform reaction caused by interfacial contaminants or native oxides.<sup>3</sup> One possible solution may be offered by materials such as Pd and Ti which are known to dissolve the native oxide layer to produce an intimate contact to silicon.<sup>4-6</sup> Interfacial contaminants remain as a major cause of high-contact resistance in various shallow contact schemes where only  $\sim 100$  Å of substrate Si is consumed.<sup>7</sup> Interfacial contaminants stay close to the active area even after silicide formation. The understanding of the effects of such contaminants is thus important for device quality considerations.

Recently, various studies approached this problem by introducing specific types of impurity elements such as oxygen and nitrogen into silicide forming systems.<sup>8-11</sup> Various aspects such as the subsequent motion of the impurities during silicide formation, their effects on silicide growth kinetics and phases formed, compound formation involving the impurity element, and electrical properties of the resultant material have been modeled and analyzed in detail. Due to the wide range of diffusivity, solubility, heats of formation of competing compounds for different impurity-host combinations, a large variety of reaction modifications and final sample configurations can be observed. Some results have led to suggestive possibilities of making shallow contacts<sup>12</sup> and diffusion barriers<sup>13</sup> using impurity controlled behaviors of metal-silicon couples.

Previous work has shown that Pd is very permeable to ambient oxygen.<sup>14</sup> However, O incorporated in Pd does not alter the  $\text{Pd}_2\text{Si}$  growth kinetics. The present work addresses the effect of another common impurity, nitrogen, on Pd silicide formation, and reports additional results obtained for oxygen impurities. To model the behavior of nitrogen and

oxygen in silicide forming systems, it is necessary to identify the moving species during the reaction. For  $\text{Pd}_2\text{Si}$ , the moving species has been a perplexing issue.<sup>14</sup> For this work, the authors shall refer to the W marker results of Ho *et al.*,<sup>15</sup> which identify Si as the dominant moving species for Pd silicide formed from amorphous Si.

## II. EXPERIMENTAL PROCEDURES

For experiments in which nitrogen was implanted into Pd, Pd films were evaporated either on an  $\langle 100 \rangle$  Si wafer or on amorphous Si evaporated on an oxidized Si wafer. The  $\langle 100 \rangle$  Si substrate was a commercially polished, *n*-type wafer, with a resistivity of 0.005–0.02  $\Omega$  cm. The Pd film thicknesses were 4030 and 1830 Å, respectively, on the above two types of Si. The evaporated Si film was 2600 Å thick. The rare nitrogen isotope  $^{15}\text{N}$  was implanted into the Pd film at energies of 300 and 200 keV/ $\text{N}_2^+$ , with calculated ranges of  $R_p = 1325$  and 866 Å, respectively. The  $R_p$  values were verified by experimental measurements. Implantation doses were 0.5, 1, and  $2 \times 10^{16}$  N/cm<sup>2</sup> for Pd on  $\langle 100 \rangle$  Si and a single dose of  $2 \times 10^{16}$  N/cm<sup>2</sup> for Pd on amorphous Si. Silicide formation was thermally induced at annealing temperatures of 250 and 200 °C for these two sets of samples.

To study the effects of O in Pd, we evaporated 1700 Å of Pd on  $\langle 100 \rangle$  Si substrate of the type described in the last paragraph. Implantation of the rare isotope  $^{18}\text{O}$  was performed at an energy of 260 keV/ $\text{O}_2^+$  to obtain a calculated projected range of 1010 Å. A single dose of  $2 \times 10^{16}$ /cm<sup>2</sup> was used, and samples were annealed at 250 °C.

To study the effects of nitrogen and oxygen implanted into Si, 1860 Å of amorphous Si was evaporated on 2900 Å of Pd, which was itself evaporated first on an oxidized Si wafer. Nitrogen and oxygen in doses of 0.5, 1, and  $2 \times 10^{16}$ /cm<sup>2</sup> were implanted at an energy of 80 keV/ $\text{N}_2^+$  or  $\text{O}_2^+$ , with an expected projected range of 1040 and 890 Å, respectively. The annealing temperature used was 230 °C for N-implanted samples and 225 °C for O-implanted samples.

Both the oxidized and bare wafers were ultrasonically cleaned before loading into the evaporation system in trichloroethylene, acetone, and methanol sequentially for 5 min

each. The bare Si substrate was, in addition, etched in 20% dilute HF solution, then immersed in an RCA solution ( $\text{H}_2\text{O}_2 : \text{NH}_4\text{OH} : \text{H}_2\text{O}$  in the ratio of 1 : 1 : 5), and finally another etch in 6% HF.

Annealing was done in a vacuum furnace pumped to  $5 \times 10^{-7}$ -Torr pressure. Evaporations were performed in an oil-free  $e$ -gun system at a pressure of  $4 \times 10^{-7}$  Torr. The deposition rate for both Pd and Si was  $20 \text{ \AA/s}$ . The silicide thicknesses were monitored by 2-MeV  $^4\text{He}^+$  backscattering spectrometry at a detector angle of  $170^\circ$ . Nitrogen and oxygen impurities were profiled using the  $^{15}\text{N}(p,\alpha)^{12}\text{C}$  and  $^{18}\text{O}(p,\alpha)^{15}\text{N}$  nuclear reaction techniques. Samples were tilted at  $60^\circ$  against normal incidence to enhance the depth resolution to  $\sim 300 \text{ \AA}$ . The proton incident energy was set at 1 MeV for  $^{15}\text{N}$  activation and 0.75 MeV for  $^{18}\text{O}$  activation. The detector was mounted in the plane defined by the sample normal and the proton beam, at an angle of  $164^\circ$  with respect to the incident beam, opposite to the direction of the sample tilt. Since  $\text{Pd}_2\text{Si}$  formation is already a well-understood process, phase identification by x-ray diffraction was not performed in this study.

### III. RESULTS AND DISCUSSION

#### A. Nitrogen in Pd

Growth curves of  $\text{Pd}_2\text{Si}$  for  $\langle 100 \rangle$  crystalline Si and amorphous Si at temperatures of 250 and  $200^\circ\text{C}$ , respectively, are shown in Fig. 1. Both unimplanted samples show

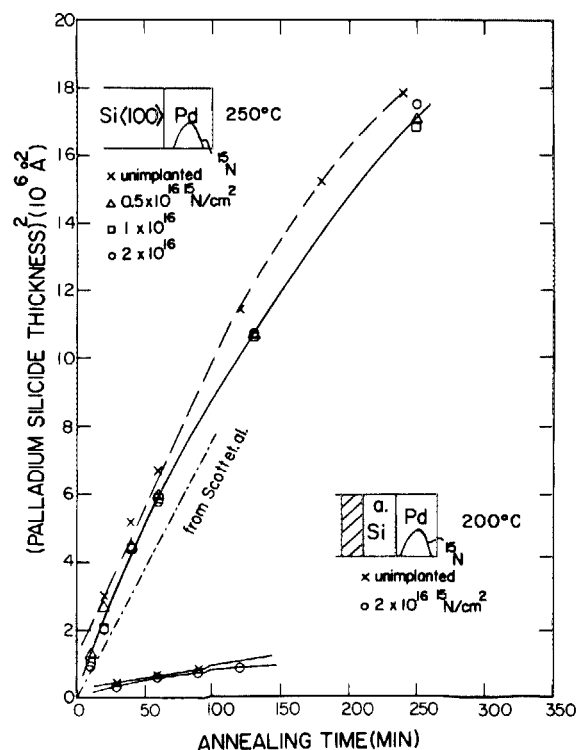


FIG. 1. Top set of curves: Thickness of  $\text{Pd}_2\text{Si}$  growth on  $\langle 100 \rangle$  Si substrates, from Pd films annealed at temperature of  $250^\circ\text{C}$ . Samples implanted with N show a very similar growth rate as the unimplanted reference. The curvature at large silicide thicknesses may be due to heavy oxygen contamination near the Pd surface. Bottom set of curves: experiment repeated at  $200^\circ\text{C}$  with a single implantation dose of  $2 \times 10^{16} \text{ N/cm}^2$  and using amorphous Si. Implanted sample also shows a similar growth rate as the reference.

initial  $\sqrt{t}$  growth rates with nonzero intercepts when the straight lines are extrapolated to  $t = 0$ . The slope of the line for  $250^\circ\text{C}$  agrees well with that of Scott and Nicolet.<sup>14</sup> When the silicide thickness exceeds  $\sim 3500 \text{ \AA}$ , a slowing of the reaction rate is observed. This may be caused by either a large stress or the huge concentration of oxygen which permeates throughout the top region of the Pd film.<sup>14</sup> The N-implanted samples systematically show slightly slower growth rates compared to the reference sample. However, the thickness difference between implanted and unimplanted samples does not exceed experimental uncertainty until  $\text{Pd}_2\text{Si}$  thickness is above  $2500 \text{ \AA}$ . Any dose dependence is too slight to be resolved from the uncertainty level of the experimental data.

In Fig. 2, the N profiles in the Pd/amorphous Si sample at various stages of the thermal treatment are given by superimposing the Pd peak of backscattering spectra with the nuclear reaction spectra for nitrogen. The horizontal axis is labeled in energy of the backscattered  $\alpha$  particle from the Pd in the sample. The energy scale for the  $^{15}\text{N}$  nuclear reaction has been adjusted so that the depth scale for the NR spectrum is the same as for the RBS Pd spectrum.

When the Pd film is partially reacted into  $\text{Pd}_2\text{Si}$ , some N is rejected from the silicide into the Pd side of the Pd/silicide interface. The rejection occurs for as long as pure Pd is being consumed by the reaction, until finally nitrogen is pushed to the Pd surface and exits from the film, resulting in 36% loss in total quantity. The residual N content in the silicide amounts to 0.7 at. % (0.7 N per lattice atom in  $\text{Pd}_2\text{Si}$ ) and is uniform throughout the layer. The completely reacted sample was annealed at  $225^\circ\text{C}$  instead of the previous temperature of  $200^\circ\text{C}$  to shorten the annealing time.

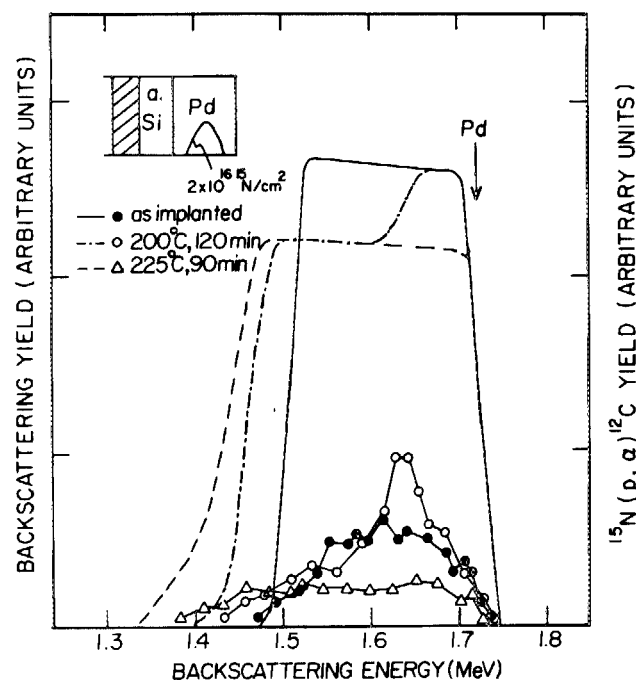


FIG. 2. Nuclear reaction signals of nitrogen superimposed on Pd backscattering peak. Nitrogen piles up at the advancing Pd/silicide interface until it exits through the top surface at the completion of Pd consumption. There is no nitrogen loss at the intermediate stage of annealing.

For comparison, we note that when N is implanted into Pt rather than Pd, the subsequently formed  $\text{Pt}_2\text{Si}$  is totally free of N.<sup>16</sup> This result is consistent with the fact that Pt is the moving species<sup>17</sup> and does not carry N with it during its diffusion across the silicide layer. This comparison strongly suggests that Pd is not the dominant moving species in the  $\text{Pd}_2\text{Si}$  formed in our experiment. The preceding paper<sup>15</sup> demonstrates that Si is the moving species in  $\text{Pd}_2\text{Si}$  formation except when the diffusion of Si is impeded. In our case, we conclude that any possible hindrance of Si diffusion is very slight in view of the unchanged silicide growth rate. We therefore approach the following analysis with the well-supported premise that Si is the moving species.

If implanted nitrogen is strongly bonded to the Pd lattice, the moving Si should diffuse around nitrogen and cause it to be incorporated into the growing silicide layer. However, Fig. 2 clearly shows that N is partially "snow-plowed" rather than completely incorporated. This is consistent with that fact that Pd does not have nitride phases,<sup>18</sup> since nitrides are less likely to be mobile than nitrogen atoms in the Pd lattice. This "snow-plow" effect may indicate that the solubility limit of N in Pd is much larger than that in  $\text{Pd}_2\text{Si}$ . Interfacial drag may be another mechanism which can explain the segregation effect. However, it is not clear whether an interfacial drag can have the same effect on bulk impurities as on interfacial impurities. These results are closely analogous to N behaviors in the Ta/Si system, where it is suspected that the metal forms a nitride only at large N concentrations.<sup>8</sup> As a last comment, we can suppose the Pd motion does contribute a minor fraction of the mass transport. Some N will be left behind by Pd and will accumulate at the Pd/ $\text{Pd}_2\text{Si}$  interface. This N will then be incorporated or segregated by the dominant flux of Si, leading to the same end picture. Therefore, the possibility of a minor Pd diffusion cannot be excluded.

## B. Oxygen in palladium

A  $\text{Pd}_2\text{Si}$  growth curve at 250 °C for a sample with O implanted into Pd is shown in Fig. 3, along with that of the corresponding unimplanted reference sample. It is apparent

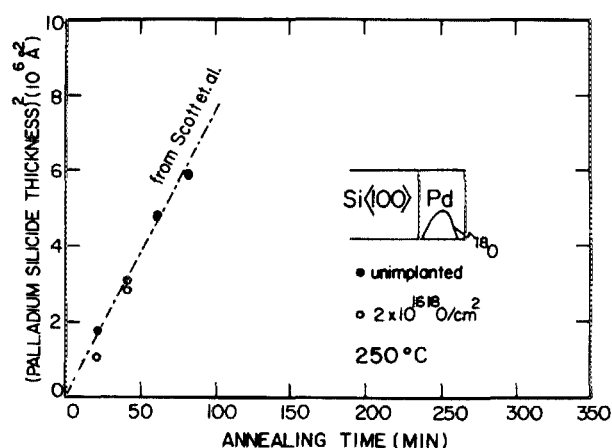


FIG. 3. Oxygen implanted in Pd does not interfere with  $\text{Pd}_2\text{Si}$  growth rate. The growth rate found in this study coincides very closely with that of Scott *et al.*<sup>14</sup>

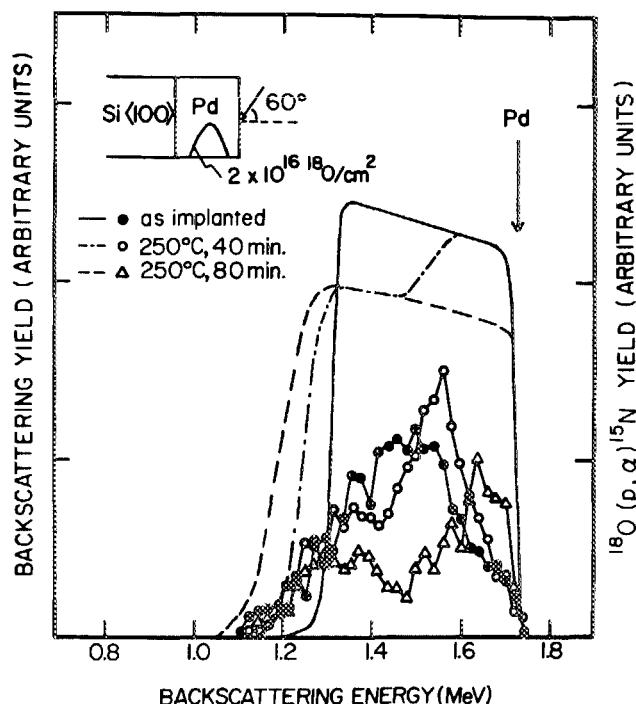


FIG. 4. A segregation effect of O in Pd is observed during  $\text{Pd}_2\text{Si}$  formation. The silicide lattice incorporates an average O concentration of 0.9 at. %. Most of the remaining O accumulates in a large surface peak when silicide formation is completed. Samples are tilted 60° against normal during backscattering.

that implanted O has no effect on  $\text{Pd}_2\text{Si}$  growth rate. This is to be expected in view of the large amount of  $^{16}\text{O}$  that penetrates into Pd during annealing<sup>14</sup> anyway. Both reference and implanted samples reproduced the growth rate reported by Scott and Nicolet.<sup>14</sup> The slight difference between the growth rate of the reference sample in this set and that in the N-implanted set may be due to the factor of 2.4 in thickness ratio combined with the huge surface O content.

The evolution of the O profile indicates a strong segregation effect (see Fig. 4) very similar to that of implanted N. However, after the silicide formation reaches completion, oxygen distinguishes itself from nitrogen in that a major portion of the residual amount of oxygen resides in a large surface peak with only 15% loss in total quantity; as compared to the N case, where all residual amount in excess of the 0.7 at. % that is uniformly incorporated in the silicide diffuses out of the sample. It can be conjectured that the thin O-rich layer, reported by Scott and Nicolet,<sup>14</sup> at the sample surface may be capturing oxygen while allowing free passage of N. The amount of O incorporated in the silicide, neglecting the surface peak, has an average concentration of 0.9 at. %. Finally, it should be mentioned that a different pattern of O redistribution was reported by Scott and Nicolet.<sup>14</sup> The causes for the discrepancies still remain to be resolved.

## C. Nitrogen in silicon

Figure 5 shows  $\text{Pd}_2\text{Si}$  growth curves for implanted and as-deposited reference samples which have evaporated Si on top. The reference sample has a  $\sqrt{t}$  growth rate. Whether a deviation from this growth pattern occurs for this reference

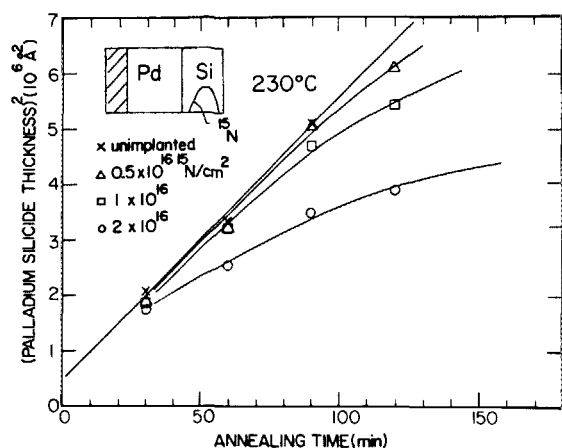


FIG. 5.  $\text{Pd}_2\text{Si}$  growth curves at 230 °C with nitrogen implanted into the top Si layer. The growth rate is increasingly severely retarded for increasing N dose. For the dose of  $2 \times 10^{16}/\text{cm}^2$ , silicide growth virtually comes to a halt after  $\sim 2000$  Å.

sample at larger silicide thickness was not tested. It is expected that the Pd film is relatively free of oxygen contamination due to the top layer of Si acting as a cap. The silicide growth rate is clearly reduced by the implanted N. At the high dose of  $2 \times 10^{16}$  N/cm<sup>2</sup>, the sample does not react beyond 2430 Å of silicide after a 580-min anneal at 230 °C. If the silicide reaction is unhindered, a 3910-Å-thick  $\text{Pd}_2\text{Si}$  layer can be formed from the evaporated Si. The N profile after this annealing step is shown in Fig. 6 as open circles. It can be seen that even though the Si/silicide interface has advanced a little beyond the peak of the nitrogen profile, there is no detectable change in the shape of the N profile. This is consistent with the notion that a partial participation of Pd in the mass transport has begun, since, if only Si moves, nitrogen that is left behind is expected to pileup at the Si/silicide interface. The role conversion of Pd from a stationary spe-

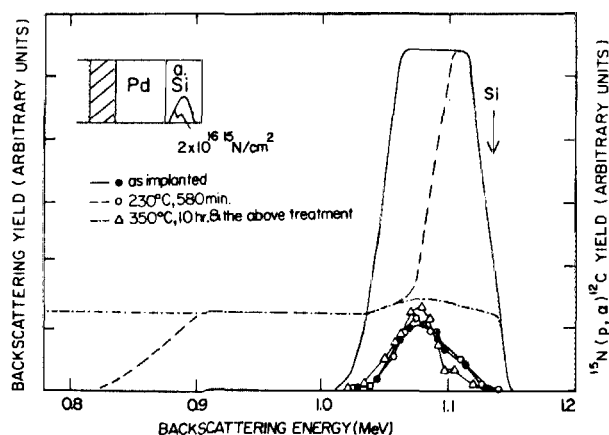


FIG. 6. With N implanted into Si, silicide reaction stops at the N-rich region after 580-min annealing at 230 °C.  $\text{Pd}_2\text{Si}$  reaction can be forced to completion by raising annealing temperature to 350 °C. There is a slight bump in the backscattering signal of Si at the near-surface region. The relative movement of nitrogen signals indicate a complicated scheme of mass transport in which both Pd and Si diffusion contribute to the growth of the silicide. The backward shift of nitrogen signal in the fully reacted sample can be explained by a predominant Pd motion during the final stage of annealing.

cies to a moving species has been observed in the preceding paper where the normal flow of Si is obstructed.<sup>15</sup>

Further reaction of the sample can be forced by raising the annealing temperature to 350 °C and annealing for 10 h longer. The silicide reaction is completed after this thermal treatment as shown in Figs. 6 and 7. In Fig. 6, there is a bump on the backscattering signal of Si in  $\text{Pd}_2\text{Si}$  indicating a slight excess of Si in the near-surface region. At the corresponding position in Fig. 7, the signal of Pd in  $\text{Pd}_2\text{Si}$  shows a significant dip. The superpositioned nitrogen signals in this spectrum show that it is this excess nitrogen (and Si) in this region that is responsible for the drop in Pd signal. The N peak concentration after the complete reaction is  $\sim 6.3$  at. %. By assuming the stoichiometric ratio of N:Si = 4:3 (for  $\text{Si}_3\text{N}_4$ ) and Pd:Si = 2:1 (for  $\text{Pd}_2\text{Si}$ ), the lowering of the Pd concentration because of  $\text{Si}_3\text{N}_4$  competing for Si is calculated to be 9.5 at. %. This is close to the value of 8.7 at. % measured for the dip in the Pd peak. Thermodynamics favors the formation of  $\text{Si}_3\text{N}_4$  ( $\Delta H_f = -25.6$  kcal/g atom or  $-59.7$  kcal/Si atom)<sup>19</sup> over that of  $\text{Pd}_2\text{Si}$  ( $\Delta H_f = -19.1$  kcal/g atom or  $-28.6$  kcal/Si atom)<sup>20</sup> in support of the above assumptions.

The complete reaction at 350 °C causes an interesting alteration of the nitrogen profile, shown in Fig. 6. The profile narrows and the peak value rises. This change is consistent with an initially predominant Si motion. The entire profile is translated toward lower-energy direction, which agrees with a predominant Pd mass transport during the end stage of the silicide reaction. The ability for Pd to convert into the moving species and consume the Si buried behind an inert barrier is unique, and has been observed in other studies where a diffusion barrier exists and a high annealing temperature

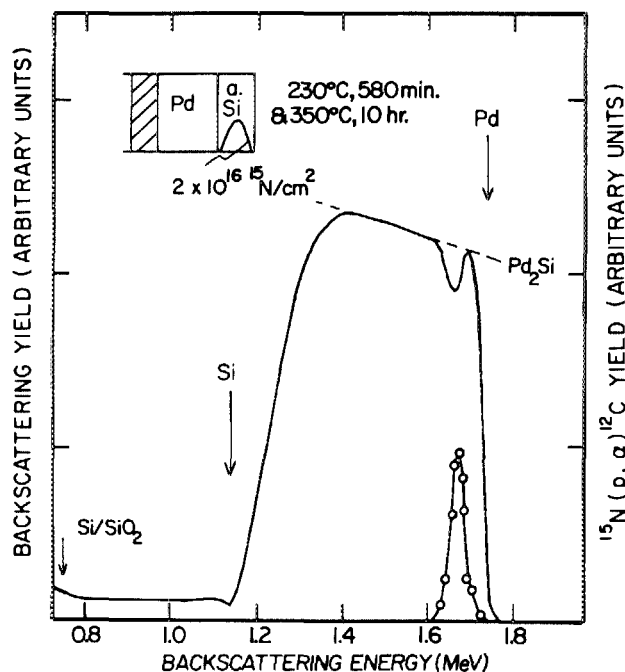


FIG. 7. A dip in the Pd peak of the  $\text{Pd}_2\text{Si}$  layer coincides in position with the peak of the incorporated nitrogen. Calculation supports the assumption that the dip is caused by a depletion of Pd concentration in the region where Si is occupied by N due to the completing  $\text{Si}_3\text{N}_4$  formation.

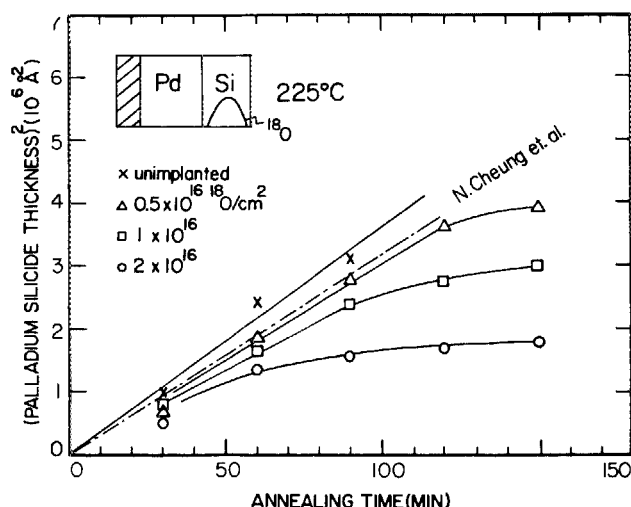


FIG. 8. Oxygen implanted in Si severely retards  $\text{Pd}_2\text{Si}$  growth rate. The effect of retardation is stronger with increasing O dose.

(>350 °C) is used.<sup>4,15</sup> The tendency for the nitride barrier to yield at a higher temperature contrasts with what was observed for  $\text{TaSi}_2$  formation,<sup>8</sup> where Si is also the moving species during silicide formation. When an equivalent N dose is introduced into Si, the  $\text{TaSi}_2$  reaction does not proceed even though the annealing temperature (675 °C) used was much higher than in the current study.

#### D. Oxygen in silicon

$\text{Pd}_2\text{Si}$  growth kinetics are also severely impeded when O is implanted into Si, as illustrated by Fig. 8. For an implanted dose of  $2 \times 10^{16}$  O/cm<sup>2</sup>,  $\text{Pd}_2\text{Si}$  thickness saturates at 1340 Å after 150-min annealing at 225 °C. The total thickness of  $\text{Pd}_2\text{Si}$  that can be formed from the evaporated Si is 3910 Å. The oxygen profile is unaltered after this thermal treatment. A high-temperature annealing was not pursued in this case.

#### IV. CONCLUSIONS

Nitrogen impurities in Pd or in Si have a minor retard- ing effect on  $\text{Pd}_2\text{Si}$  growth rate, which becomes more appar- ent at silicide thickness above 2500 Å. Only thin  $\text{Pd}_2\text{Si}$  layers were used for studying O effects, and no alteration of silicide growth rate was observed. Although Si is the moving species, N and O are partially "snow plowed" by the Pd/silicide in- terface. A uniform concentration of 0.7 at. % of N or 0.9 at. % of O is incorporated into the  $\text{Pd}_2\text{Si}$  lattice in each case.

All excess nitrogen is finally ejected out of the Pd film, re- sulting a 36% loss in total quantity. Most of the excess oxy- gen accumulates in a large surface peak, resulting in only 15% loss in total quantity. When included in Si, both N and O will severely retard the silicide growth. The reaction con- tinues at an elevated temperature with Pd as the diffusing species.

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